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ENERGY STORAGE AND CONVERSION IN SOLID HYDROGEN

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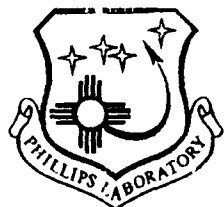
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FOREWORD

This final report was submitted by the University of Hawaii under contract F04611-88-K-0048 with the OLAC PL/RKFE Branch, at the Phillips Laboratory, Edwards AFB CA 93524-7680. OLAC PL Project Manager was Dr Stephen Rodgers.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the SF Form 298.

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13. ABSTRACT (MAXIMUM 200 WORDS) The trapping of unpaired atoms of hydrogen (H) in a solid hydrogen matrix (H ₂) increases the energy available for propulsion applications, i.e. the specific impulse. The incremental increase in stored energy depends on the metastable atomic hydrogen concentration. To maintain a large atomic hydrogen concentration, recombination of atoms into molecules must be understood and suppressed. It was the purpose of this research to study both theoretical and experimental approaches to creating large atomic hydrogen concentrations. The theoretical considerations have lead to analytic procedures for calculating the atom diffusion times and the atomic recombination coefficients from statistical mechanics. The experimental studies have yielded numerical estimates of the atom density in solid tritium based on measurements of the ortho to para tritium conversion rate. The atom density expressed as a concentration approaches 1% near K. Such large atom densities lead to very unusual thermal response when the temperature of the host solid matrix is increased, resulting from the rapid recombination of the trapped atoms. In practice, this response provides a method of retrieving the stored energy from the host solid.				
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Symbols and Abbreviations

isp.	the specific impulse, the ratio of the force to the weight loss per unit time
W	weight loss per unit time
g	acceleration due to gravity at the earth's surface, 9.8 m/s^2
E	energy
m	mass
p	linear momentum
h	external magnetic field in units of energy
s(i)	spin variable to describe lattice occupancy
μ	chemical potential for a fixed number of atoms
J_0	magnetic exchange interaction
V_0	nearest-neighbor van der Waals interaction
n_{ave}	average number of atoms per unit volume
$\delta(t)$	Dirac delta function
α_0	bimolecular recombination coefficient
D_0	atomic diffusion coefficient
r_0	Onsager kinetic coefficient
m	atomic hydrogen density
K	atom production rate
EA	activation energy for diffusion
x_1	ortho H_2 concentration
k	ortho H_2 decay constant
W_{10}	transition probability per unit time from $J=1$ to $J=0$ level
W_{01}	transition probability per unit time from $J=0$ to $J=1$ level
R	ortho-para conversion rate
c	concentration of unpaired electron spins
Ω	conversion rate for a single molecule next to an electron spin
z	number of neighboring sites
Γ	atom hopping rate
$\Delta\omega$	Electron Spin Resonance linewidth
ω_d	average local magnetic field
ppm	parts per million

SUMMARY

Our previous experimental and theoretical work on atoms in solid H_2 leads to the conclusions: (i) that large concentrations of atoms can exist in molecular solids at low temperatures; (ii) that it is easier to cool samples with known radioactivity than might be imagined; (iii) that the atoms are inhomogeneously distributed throughout the sample; and (iv) that application of a magnetic field may increase the concentration of atoms that can be stored at a given temperature or their storage time.

The goals of maximizing the stored energy and determining the conditions needed for storing the energy for a specified period of time are within reach but future work is suggested. These experiments will explore methods of producing atoms in solid hydrogen and methods to quantify and stabilize atomic hydrogen concentrations.

The experiments proposed here for future studies will directly measure the energy stored in the solid host by "thermal analysis"; the ratio of the light energy emitted during recombination to the total energy released; the magnetic susceptibility of the atoms (plus any other magnetic excitations); the times for atom equilibration following a triggered energy release; and the effects of a magnetic field on the energy storage times. *An alternative method of producing atoms in solid hydrogen will be explored.* Electron bombardment of hydrogen samples will be attempted.

A search through the "parameter space" of magnetic field (H) and temperature (T) should be made in order to optimize the equilibrium density of atoms that can be stored in molecular solids--at temperatures and fields of practical interest.

This report is organized in the following manner: the technical accomplishments are divided into the categories (i) an introduction; (ii) theoretical developments; and (iii) analysis and modeling of the experimental results. Suggestions for future work are included in the Conclusion. The P.I.s were Dr. James R. Gaines and Dr. C.A. Vause, III, University of Hawaii at Manoa.

INTRODUCTION

Hydrogen burned in oxygen is today's benchmark fuel for rockets. The physical quantity used for fuel comparisons is the "specific impulse" defined to be the ratio of the thrust (in lbs) to the weight loss per unit time (in lbs per sec). This quantity has dimensions of time and is measured in seconds. The burning of H_2 in O_2 produces a specific impulse of 400 to 440 seconds. A 10% increase in specific impulse would be important to rocket designers.

Specific Impulse Calculations

One quantity that can be used for the comparison of rocket fuels is the "specific impulse", I_{sp} . This quantity is defined as the ratio of the force to the weight loss per unit time.

$$I_{sp} = \frac{\text{Force}}{\dot{w}} = \frac{\left[\frac{\Delta p}{\Delta t} \right]}{\left[\frac{\Delta w}{\Delta t} \right]} = \frac{\Delta p}{\Delta w} \quad (1)$$

In this expression, the final result depends only on the ratio of the change in linear momentum Δw , the increment in time Δt over which these changes take place has cancelled out.

Using classical physics, the above expression can be modified to produce one that is very useful for calculations where the energy (E) produced by some reaction involving the loss of weight $\Delta w = (\Delta m)g$ is known. Here g is the acceleration due to gravity at the earth's surface, 9.8 m/s^2 . Since the linear momentum (p) is related to the kinetic energy by:

$$p^2 = (2m)E$$

we can write $\Delta p = (2\Delta m E)^{1/2}$ so the specific impulse becomes:

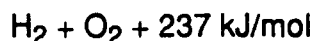
$$I_{sp} = \sqrt{\frac{2(\Delta m)E}{(\Delta m)^2 g^2}} = \frac{1}{g} \sqrt{\frac{2E}{\Delta m}} \quad (2)$$

This formula will be applied to three special cases.

Applications of Specific Impulse Calculations

Three applications are given below to illustrate the use of the specific impulse calculations. These examples are: the "benchmark fuel" of hydrogen burning in oxygen; recombination of pairs of atoms stored in solid hydrogen; and a "nuclear" fuel based on the tritium beta decay.

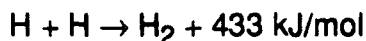
The Water Rocket. The "water rocket" where H_2 is combined with O_2 to produce H_2O . The reaction



is the benchmark for rocket propulsion. For substitution into Eqn. 2, we use $E = 2.37 \times 10^5 \text{ J/mol}$ and $\Delta m = 0.018 \text{ kg/mol}$ to obtain

$$I_{sp} = 524 \text{ sec.}$$

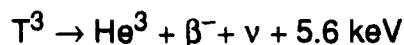
The Chemical Rocket. Another example of a "chemical rocket" is based on the recombination of hydrogen atoms into a molecule where 4.5 eV is released per event.



For this case, $E = 4.5 \times 10^{-19} \text{ J}$ and $\Delta m = 0.002 \text{ kg/mol}$ so

$$I_{sp} = 2.12 \times 10^3 \text{ sec.}$$

The Tritium Rocket. The tritium rocket would derive its energy from the beta decay of the tritium atom, each such beta decay giving an average kinetic energy of 5.7 keV.



This particular "nuclear rocket" does not produce undesirable waste products and so might be usable without polluting space. For this example, using a mole of T_2 with its mass of 0.006 kg/mol and $E = 1.1 \times 10^9 \text{ J/mol}$, we obtain for the specific impulse,

$$I_{sp} = 6.17 \times 10^4 \text{ sec.}$$

In conclusion, the water rocket based on the combustion of hydrogen in oxygen is the standard of comparison for rocket propulsion.

Two examples have been cited that have higher theoretical performance than the standard. The hydrogen atom recombination rocket is a factor of four better than the water rocket. The tritium rocket is a factor of one hundred better than the water rocket and does not have objectionable by-products.

The very large calculated specific impulses in the last two examples are responsible for the interest in hydrogen. Utilization of such increases in specific impulse will depend on being able to create large densities of atomic hydrogen in solid molecular hydrogen so that the burn time can be sufficiently long and then to store those atoms until the power is needed. These are the essential scientific problems addressed by the present research contract.

THEORETICAL DEVELOPMENTS

Statistical Mechanics can be used to calculate atom dynamics. We have completed preliminary studies on the problems related to hydrogen storage in the equilibrium and nonequilibrium regimes. These are presently being organized into several manuscripts to be submitted for publication. A summary is presented below.

Equilibrium Statistical Mechanics

The equilibrium study involves an investigation of the magnetic properties of the stored atoms. The assumptions of the particular model studied are that (a) by some external means a fixed population of atoms is stored, (b) that the system is in thermal equilibrium under the applied constraints (this is more properly a macroscopic state of partial equilibrium since upon removal of the external constraints, namely the sources of atom production, the system will have the tendency to eliminate atoms through recombination processes), and (c) that the host lattice's role is to provide sites (vacant cells) for atoms and mediates the effective interactions between the atoms (via short-ranged potentials), however, is passive otherwise. The sites are either occupied by an atom or not (vacancy), and if an atom is present, there is a magnetic moment with two degrees of freedom aligned uniaxially "up" or "down" with respect to some quantization axis. These states are quantified in the model by a classical "spin-one" variable at each site i , $s(i) = -1, 0, 1$. The atomic occupancy at each site is given by $s(i)^2 = 1$, the magnetic states are $s(i) = -1, 1$. We study the simple lattice model Hamiltonian of such a classical spin-liquid

$$H = -h \sum_i s(i) + \mu \sum_i s(i)^2 - J_0 \sum_{\langle ij \rangle} s(i)s(j) - V_0 \sum_{\langle ij \rangle} s(i)^2 s(j)^2 \quad (3)$$

in the mean-field (MF) approximation. The parameters in the model are the external magnetic field (in energy units) h , the chemical potential for the fixed number of atoms μ , the nearest-field $\langle ij \rangle$ magnetic exchange interaction J_0 , and the nearest neighbor attractive van der Waals interaction V_0 . (The repulsive part is contained in the constraint

that no more than one atom can occupy a site.) A model similar to the above was proposed by Blume-Energy-Griffiths [1] for the study of ^3He - ^4He mixtures in which the parameter-space had a completely different meaning than in our case. The phase diagram and magnetic susceptibility has been calculated in the MF approximation, the details of which are to be published. Qualitatively, the model indicates that there is a magnetic phase transition coupled with a liquid-gas transition for some range of the ratio J_0V_0 . This may be related to the observation reported by Webeler's experiment [2] in which it was found that the magnetic susceptibility cannot be explained by a paramagnetic model alone, and speculated that ferromagnetic domains may exist. We plan to continue this study by including fluctuations in both the density and magnetic parts which are neglected in the MF analysis and are known to be essential in critical phase transitions.

Non-Equilibrium Statistical Mechanics

The nonequilibrium study has focused on the investigation of deriving the macroscopic kinetic equation for the number of stored hydrogen atoms in its molecular solid host in a hydrodynamic approximation in which diffusion, recombination, and density fluctuations are taken into account. The conventional gas-phase macroscopic kinetic equation is taken to be of the form [3]

$$dn_{\text{ave}}(t)/dt = -\alpha_0 n_{\text{ave}}(t)^2 + n_0 \delta(t) \quad (4)$$

for a unit impulse source where $n_{\text{ave}}(t)$ is the average number of atoms per unit volume V of the system, N_0 is the number of atoms per unit volume produced at $t=0$, and α_0 is the bimolecular recombination coefficient. Diffusion is then via the ad hoc assumption that $\alpha_0 \propto D_0$, where D_0 is the atomic diffusion coefficient [3,4]. This macroscopic equation already assumes that an averaging over statistical fluctuations at temperature T has been carried out. Our approach, on the other hand, has been to derive the macroscopic kinetic equation by beginning from a more fundamental level where one starts with a local fluctuating atomic density $n(\mathbf{r},t)$, at position \mathbf{r} . The average particle density is then obtained from

$$dn_{\text{ave}}(t)/dt = (1/V) \int d^3r \langle n(\mathbf{r},t) \rangle \quad (5)$$

where $\langle \dots \rangle$ denotes the statistical averaging over density fluctuations consistent with the fluctuation-dissipation theorem [5]. Such a "hydrodynamic approach" contains diffusion and recombination effects in a natural manner. detailed theoretical analysis (which is considerable and will be published elsewhere) produces the macroscopic kinetic equation

$$dn_{\text{ave}}(t)/dt = An_{\text{ave}}(t)/dt - \alpha_0 n_{\text{ave}}(t)^2 + n_0 \delta(t) \quad (6)$$

where

$$A = (\sqrt{2}\alpha_0^2\gamma_0/4\pi D_0^{3/2})^{2/3} \quad (7)$$

with γ_0 the Onsager kinetic coefficient [5]. Hence, fluctuations change the macroscopic kinetics by dynamically generating a first-order term. An analysis of a microscopic lattice model which has the identical hydrodynamic limit of reveals that α_0 is *not* proportional to D_0 as is assumed in the ad hoc model in the conventional theory [3,4].

We have been able to compare the above theory with experiments by G. W. Collins [6] on $H_2 + 2\% T_2$ at $T = 1.4$ K and find that fits to the data reveal $A = 0$. Such a fit is shown in Figure 1 with $A = 6.1 \times 10^{-6} \text{ sec}^{-1}$, and $\alpha_0 = 4 \times 10^{-26} \text{ cm}^3\text{-sec}^{-1}$.

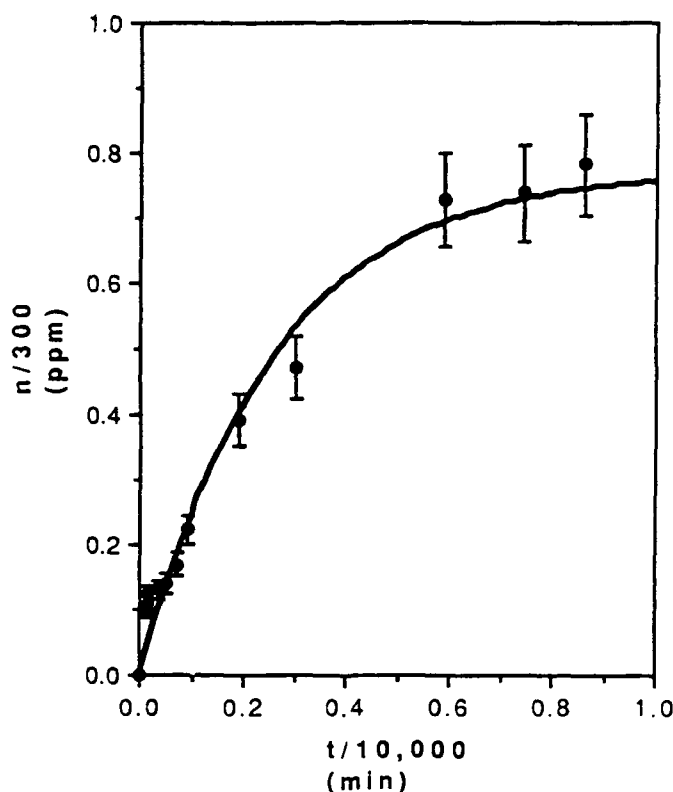


Figure 1

The normalized atom concentration for $H_2 + 2\% T_2$ at $T = 1.4$ is plotted as a function of the normalized time. To scale the atom concentration, it is divided by the concentration of 300 ppm (parts per million) while the actual time is divided by 10,000 minutes. The solid curve was calculated theoretically from Eqn. 6 with $A = 6.1 \times 10^{-6} \text{ sec}^{-1}$ and $\alpha_0 = 4 \times 10^{-26} \text{ cm}^3\text{-sec}^{-1}$, while the filled circles are data from Ref. 6.

The macroscopic kinetic theory could be considerably extended by including the dynamics of other degrees of freedom neglected in the analysis thus far.

ANALYSIS AND MODELING OF THE EXPERIMENTAL RESULTS

The solid hydrogens, especially at zero applied pressure, have been extensively studied and will be regarded as a well characterized "host" for the storage and study of atomic excitations trapped in the lattice structure. In contrast, there are very few experimental studies (and no prior theoretical studies) of the solid hydrogen hosts after irradiation has produced atoms in the solid prior to the present work of LLNL and University of Hawaii collaboration. Using the facilities in the Tritium Building at LLNL, experiments on NMR, thermal conductivity, ESR, optical and thermal studies on solid T₂ and D-T [6-11] have been completed. Three previous experiments: (i) the study by Sharnoff and Pound [12] on D₂ doped with T₂; (ii) the (unpublished) experiment of Leach and Fitzsimmons [3] on molecular H₂ irradiated by 200 keV pulses of electrons from an electron gun; and (iii) the low temperature study by Webeler [2] on H₂ pulses containing trace amounts of T₂, all have contributed to our present understanding of hydrogen hosts containing unpaired atoms. Sharnoff and Pound first used ESR techniques to measure steady-state atom density in a solid hydrogen host. Leach and Fitzsimmons probed the kinetics of atom recombination in hydrogen hosts and Webeler was first to call attention to the bizarre thermal properties of hydrogen atoms stored in a hydrogen host.

A Direct Measurement of the Atom Density

Sharnoff and Pound made direct observations of the D atoms produced in solid D₂ by a small (at most 1%) impurity concentration of T₂ molecules. The β decay of the T nucleus produced D atoms which they could observe through the EPR signal with its characteristic hyperfine splitting. Because their source was so weak, they could observe the build-up in time of the atom population at 4.2 K. From our analysis, the transient response depends on both the source strength (the T₂ impurity) and the recombination coefficient. Unfortunately, neither of these quantities was extracted from this measurement since it was not known how much of the original T₂ gas actually went into the microwave cavity. By careful experimentation, it was possible to connect the EPR signal size with the actual number of atoms. They concluded that at 4.2 K they had 3×10^{17} spins in their sample from a source that at most was 1% T₂.

The Atom Recombination Coefficient in H₂

Leach and Fitzsimmons were the first to study the kinetics of atom recombination in hydrogen hosts. The pulsed electron source used by Leach and Fitzsimmons produced H atoms, easily identified in the ESR spectrum from their characteristic hyperfine splitting of 509 gauss. At a fixed sample temperature, between 8.1 K and 6.5 K, measurement of the relative EPR intensity as a function of time after the electron beam was switched off yielded the recombination coefficient $\alpha(T)$ for the atoms. This coefficient is defined by:

$$dm/dt = -\alpha(T)m^2 \quad (8)$$

where m is the atomic H concentration (in an applied magnetic field of 3 kg). As defined above, the recombination coefficient was found experimentally to be an exponential

function of the sample temperature,

$$\alpha(T) = \alpha_0 \exp(-E_A/kT) \quad (9)$$

where $\alpha_0 = 4.1 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ and $E_A/k = 195 \pm 10 \text{ K}$. Using simple arguments from kinetic theory, they deduced the diffusion coefficient for the atoms to be:

$$D_{\text{atom}} = (0.07 \text{ cm}^2 \text{ s}^{-1}) \exp(-195 \text{ K}/T). \quad (10)$$

Incidentally, the activation energy, E_A , they obtained for atom diffusion, agreed with the NMR determination of the activation energy for molecular self diffusion [3].

Low Temperature Studies of H_2 Containing T_2

Combining the ideas of Sharnoff and Pound and Leach and Fitzsimmons, suggestion that H_2 , in the presence of a constant electron flux such as that obtained with their electron gun constantly on (the equivalent of adding a positive constant (K) to the right hand side of Eqn. 1) or with an internal source such as Sharnoff and Pound used, would acquire an equilibrium number of atoms that would increase exponentially with decreasing temperature. Thus for

$$dm/dt = K - \alpha(T)m^2 \quad (11)$$

in the steady-state, the atom density (m_0) is given by:

$$m_0 = \sqrt{\frac{K}{\alpha(T)}} \quad (12)$$

The increase Webelerin m_0 would be due to the exponentially decreasing recombination coefficient so that the larger the electron flux or source strength, the larger the equilibrium number of atoms. Using the Leach and Fitzsimmons estimates of atom production with their beam on and their measured recombination coefficient gives predictions of steady-state atom concentrations at $T = 4 \text{ K}$ and below that are enormous.

Webeler was interested in using solid hydrogen to store energy, in the form of atoms. Initially, he studied a sample of solid H_2 containing 0.03% T_2 by weight. His experimental arrangement was very simple; only the sample temperature and magnetic moment were measured. About 75% of the total energy available from the β decays stayed in the sample, presumably in the form of stored atoms. Upon cooling to temperatures below 0.8 K, spontaneous energy releases were observed. It was found that at fixed temperature, the time before energy was released could be significantly increased if a magnetic field was maintained on the sample.

Another interesting feature of Webeler's work was the observation that the magnetic moment was too large to be explained by Curie Law even if all the energy available from β decays produced atoms. He concluded that there were regions of his sample that behaved like ferromagnetic domains. His experimental work, while not quantitative,

contained several novel suggestions and generated more detailed mathematical analysis by Rosen [13,14] and Zeleznik [15].

Results Obtained by the UH-LLNL Collaboration

The collaboration between scientists at Lawrence Livermore National Laboratory (LLNL) and the University of Hawaii has made several contributions to the understanding of this novel energy storage system. These contributions include: (i) the first NMR measurements of the ortho to para conversion rate in solid T_2 and D-T that were interpreted to infer the atom density as a function of temperature [16-18]; (ii) the first thermal conductivity measurements on solid T_2 and D-T that yielded detailed information about the "heat spikes" in tritiated hydrogens and provided the basis for controlling this (usually) unwanted thermal response; (iii) the first ESR measurements on solid T_2 and D-T that have given another determination of the atom density (about ten times smaller than the one from NMR data on the conversion rate) and provided insights into the kinetics of atom recombination; (iv) the first studies of the optical emission from tritiated solid hydrogens; and (v) the first theoretical work to calculate the dynamical response of atoms in a solid hydrogen host from statistical mechanics. Brief descriptions of these past contributions will be included here, partly for scientific background and partly as a progress report on the experimental and theoretical activities.

Inference of Large Atom Densities. We used NMR techniques to measure the ortho to para conversion rate as a function of temperature. In T_2 , the NMR signal is due only to those molecules with $J = 1$, $I = 1$ as only the lowest rotational level in the ortho series is occupied (with any statistical weight) below 20 K. Thus by monitoring the NMR signal as a function of time, at fixed temperature, we measured the ortho population's time dependence. We found that the ortho population followed an exponential decay in contrast to the much studied situation in H_2 where the ortho concentration (where x_1 is the $J = 1$ concentration) is characterized by:

$$dx_1/dt = -kx_1^2 \quad (13)$$

Our basic findings were:

(i) The oT_2 signal decays exponentially in time at fixed temperature indicating that the conversion is not "intrinsic" but is catalyzed. The time constant of the exponential decay, τ , was measured as a function of temperature and showed a minimum at about 11.4 K. See Figure 2.

At this minimum, the rate in T_2 is about two hundred times faster than in H_2 at zero pressure at 4.2 K so that it cannot be explained by intrinsic conversion mechanisms.

(ii) After the oT_2 signal has stopped changing in time, the remaining oT_2 concentration is larger than that predicted from the Boltzmann populations of the rotational energy levels. This can be understood by noting that recombination of two atoms into a molecule favors the excited rotational level by three to one (just the spin "weight" factors). The upper rotational level is pumped by recombination.

From the data, we were able to extract three quantities: namely the transition

probability per unit time to go from the excited rotational level to the ground state (W_{10}), the inverse probability (W_{01}), and the constant atom production rate. The result obtained for the conversion rate (W_{10}) is shown in Fig. 3. A clear maximum is seen at 11.4 K. The significance of W_{10} is that it can be calculated theoretically, as we did, for various mechanisms and then compared with the data to identify the dominant mechanism.

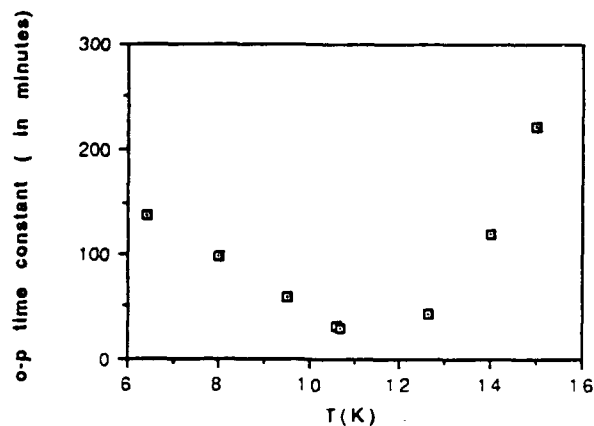


Figure 2

The time constant of the measured exponential decay, in minutes, is plotted as a function of temperature. There is a pronounced minimum at about 11.4 K.

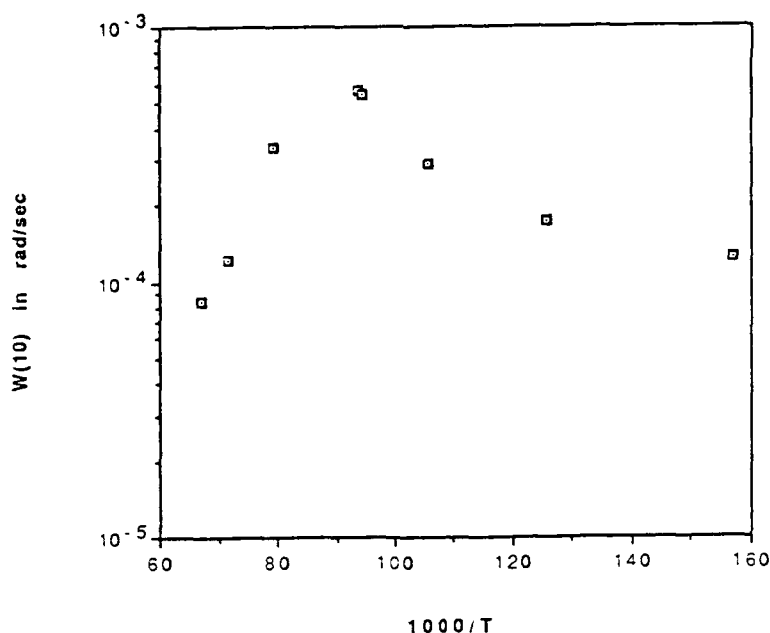


Figure 3

The derived quantity, W_{10} , the transition probability per unit time to go from the excited rotational level to the ground state is plotted as a function of the inverse temperature, $1000/T$, where the scaling factor 1000 is a conventional choice.

The conversion rate is accelerated over that expected for intrinsic conversion because there are many unpaired electron spins (atoms) in the solid. To produce a peak in the conversion rate, either the atoms or the molecules (or both) must be capable of motion. Motion of the molecules was ruled out by our (unpublished) measurements on the self-diffusion coefficient of the molecules as a function of the temperature. The effect of the motion of the atoms on the conversion rate of the molecules was treated by a "hopping model".

The conversion rate (in the low concentration limit) given by this model can be written:

$$R = c(z\Omega\Gamma/\zeta\Omega + \Gamma) \quad (14)$$

In this expression, c denotes the concentration of unpaired electron spins (atoms), Γ is the rate for an electron spin to hop to a neighboring site, s is the number of neighboring sites, and Ω is the conversion rate for a single molecule adjacent to an electron spin. The product $z\Omega$, was calculated [14] on the assumption that the atoms are in the large interstitial positions between hops to nearby interstitial positions and found to have the value $z\Omega = 14.1 \text{ s}^{-1}$ when $z = 6$. It is convenient to denote the product, the "local" conversion rate, $z\Omega$ by Ω_0 . The equilibrium atom concentration itself depends on the atom hop frequency leading to an expression for the rate in terms of the hop frequency that does have a peak in it when the hop frequency equals the "local" conversion rate. We then used the peak rate from the data to obtain the "local" conversion rate and this value agreed with our calculated value to within a factor of three. Using the local conversion rate found from the peak rate, we can then extract the hop frequency as a function of the temperature from the data. With a known hop frequency, we can calculate the equilibrium atom density. This important quantity is shown in Fig. 4. In short, the results for the hop frequency suggest that the atom gas starts out at high temperatures as "very mobile" but is localized at our lowest temperatures (about 6 K). The corresponding atom densities are very large and extrapolate to 2 to 5×10^{20} per cm^3 at 4.2 K depending on the method of extrapolation chosen. This corresponds to 0.7% to 1.7% atoms in a solid H_2 host.

Our NMR experiments, interpreted in terms of the atom density established that molecular solids such as H_2 , D_2 , and T_2 can act as hosts for large numbers of atoms.

The equilibrium atom density depends on the dynamic balance between atom production and atom recombination. Details such as the dependence of the recombination on temperature (below 6 K) and magnetic field and its relationship to the diffusion coefficient remain to be investigated. Although Webeler observed the atom "storage times" to increase when a magnetic field was used, **the optimum density of atoms that can be stored at a given temperature and magnetic field is unknown.**

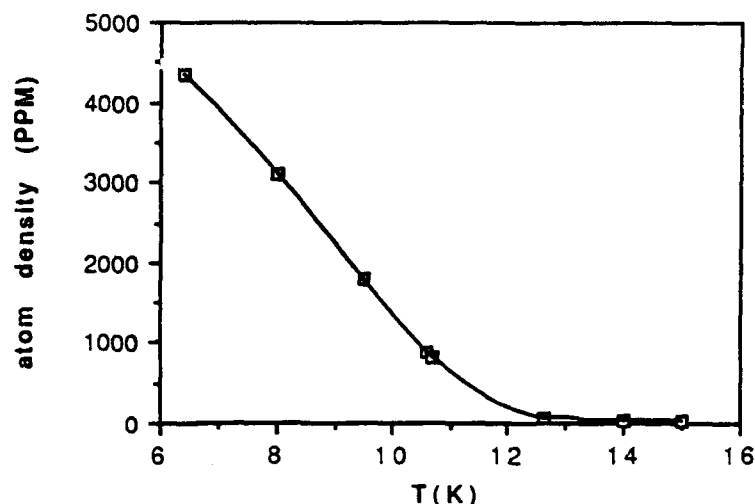


Figure 4

The equilibrium atom density (n) calculated from the o-p conversion data is plotted as a function of temperature. The corresponding atom densities extrapolate to between 2 and 5×10^{20} per cm^3 at 4.2 K, corresponding to about 1% in a solid H_2 host.

The Thermal Response. Our earlier NMR experiments had been troubled by sudden upward excursions of the sample temperature below 6 K. This effect was probed more thoroughly in the thermal conductivity experiments and the ESR experiments. The temperature excursions were called "heat spikes" and heat spikes could be either triggered by a temperature ramp or they could occur spontaneously. The thermal response is very unusual when the atom density is large.

The most elementary way of observing heat spikes is by monitoring the sample thermometer. In Fig. 5, we show the reading on a germanium resistance thermometer (a "heat spike") following a sudden increase in the sample temperature. The sample itself was 2.3 mole of solid D-T (actually 25 mol% D_2 - 50% DDT - 25% T_2) in the shape of a cylinder of 2.0 mm radius and 3.5 mm height inside a sapphire cell used for NMR measurements. In Fig. 5, the sample controller was changed from 3.7 K to 4.9 K at 15 s. The unusual thermal response is seen for a D-T sample but not for a sample of HD under the same conditions. From observations of this kind, we find that heat spikes can be triggered by a sudden increase in sample temperature or they can occur without any apparent cause, i.e., spontaneously.

During the course of the ESR measurements of the atom density, heat spikes could be observed by monitoring the sample temperature.

The most illuminating experimental observation of the heat spikes came from our X-band (9.4 GHz) electron spin resonance (ESR) experiments. The sample cell was made of sapphire in a geometry almost identical to that of the NMR cell. The average hydrogen sample size used was 2.2 mmol, so that 2 mW of radioactive decay heat was emitted from a pure tritium sample.

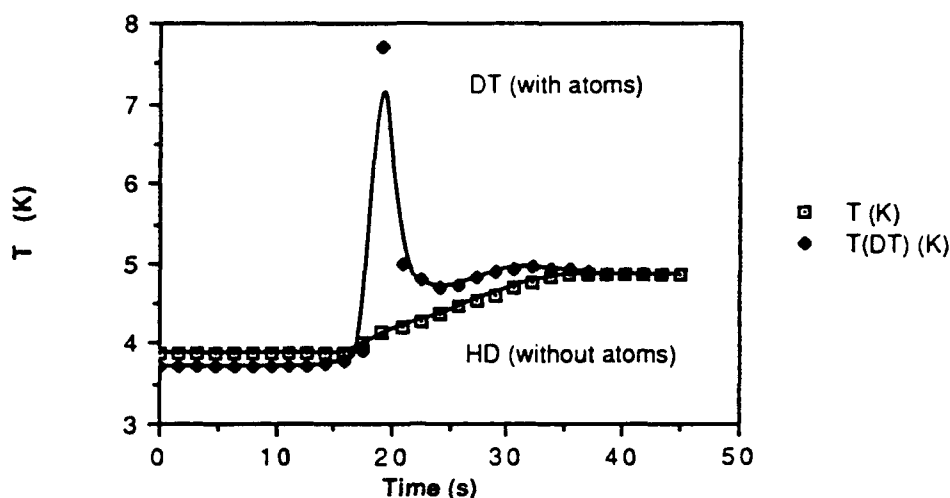


Figure 5

The thermal response following a programmed sample temperature change is shown for two different samples. The open squares represent an HD sample that contains no unpaired atoms. The sample temperature follows the temperature change from 3.7 K to 4.9 K at 15 s dictated by the sample temperature controlled. The filled squares represent the response for a D-T sample containing unpaired atoms. This is a triggered "heat spike".

By monitoring the germanium resistance thermometer on a recorder, we could tell when a heat spike occurred. For our samples containing at least 2% or tritium, the steady-state atom density, as measured by ESR increases with decreasing temperature. During the course of the ESR measurements of the atom spin density, heat spikes could be triggered. Figure 6 shows the total atom concentration in parts per million (atoms to molecules) for solid D_2 containing 2 mol% tritium as measured by ESR with times where heat spikes occur indicated.

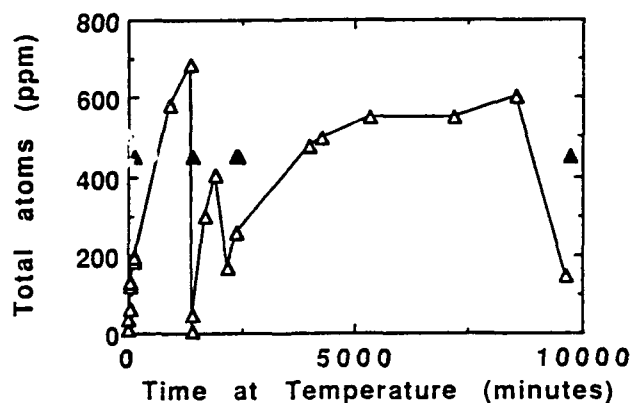


Figure 6

A "heat spike" as seen in an ESR experiment. The total atom concentration (open triangles) in parts per million (atoms to molecules) for solid D_2 containing 2 mol% tritium as measured by ESR with times where heat spikes occur indicated by the filled triangles. As a result of a heat spike the atom concentration becomes smaller.

Note that as a result of a heat spike the atom density becomes very small. We have also seen spikes in solid D-T and T_2 below 2.2 K as well as in HD containing 2% T_2 between 1.2 K and 1.4 K. Only in H_2 , to temperature as low as 1.7 K were no spikes seen. The correlation of the heat spikes with the decrease in ESR spin count indicates that the thermal spikes result from hydrogen atom recombination.

In addition to the triggered heat spikes, we also observed heat spikes when we do not intentionally trigger them. These "spontaneous" heat spikes are usually observed when at the minimum sample temperature where there is no reserve cooling power. In attempt to eliminate these spontaneous heat spikes in our ESR experiments, we filled the remaining volume of the cavity with liquid 4He . Under those conditions, the heat spikes were either unobservable or suppressed by several orders of magnitude. However, when the cavity contained only a small amount of 4He on top of the sample, we still observed heat spikes, both from the germanium resistance thermometer readings and from the vapor pressure changes of the liquid 4He above the sample, although the frequency of occurrence was reduced considerably.

The stored energy in a hydrogen host can be recovered quickly by triggering a heat spike. How much of this energy appears directly as heat and how much appears as light will be probed by our future experiments.

ESR Measurements. ESR measurements have produced detailed information about the atoms trapped in solid hydrogen hosts. The observed ESR spectrum [6] of a solid hydrogen host containing atoms is sensitive only to the atoms. The spectrum of an atom "free atom" making it possible to identify individual atoms of H, D, and T. In Figure 7, the ESR spectrum of DT at 1.6 K is shown. Both T atoms (a doublet hyperfine structure with splitting of over 500 gauss) and D atoms (a triplet hyperfine structure in the center of the T doublet) are observed. The striking unambiguous but as will be seen later, this recorded spectrum does not contain information about all of the atoms present but only those atoms that are far enough away from other atoms so that their spectrum is not broadened nor altered from the free atom spectrum. Therefore the atom density of "free atoms" which can be much smaller than the total atom density.

It is thus possible to measure the frequency shift of a given ESR line with respect to a free atom, the line width, the spin lattice relaxation times. Even now it is possible to obtain information in the lattice from their spectra and relaxation times. Even now it possible to obtain information about kinetics from the growth of the ESR signal following a heat spike or from the growth of a signal when the sample is cooled to a new lower temperature.

Following the approach of Sharnoff and Pound, the atom density was obtained in terms of the integral of the ESR lineshape. Data [6] taken on T_2 is shown in Figure 8.

The density so obtained increased with decreasing temperature as did the density obtained from the ortho to para conversion experiments. However, the density from the ESR experiments was almost a factor of ten smaller than the density from the ortho to para conversion. If we use the measured ESR linewidth to calculate the atom densities in agreement with those larger densities obtained from the ortho to para conversion.

In addition to the ESR signal strengths (and their time dependence), the spin-lattice relaxation time (T_1) and the width of the hyperfine split lines $\Delta\omega$ was measured. The increase of the line width with decreasing temperature can be interpreted as the dipolar broadening produced by other atoms. Treatment of the line shape problem at very dilute concentrations of spins is difficult since it is the nearest neighbor that has the strongest influence on the width, dictating a statistical treatment. Apart from details, the linewidth can be written in this limit as:

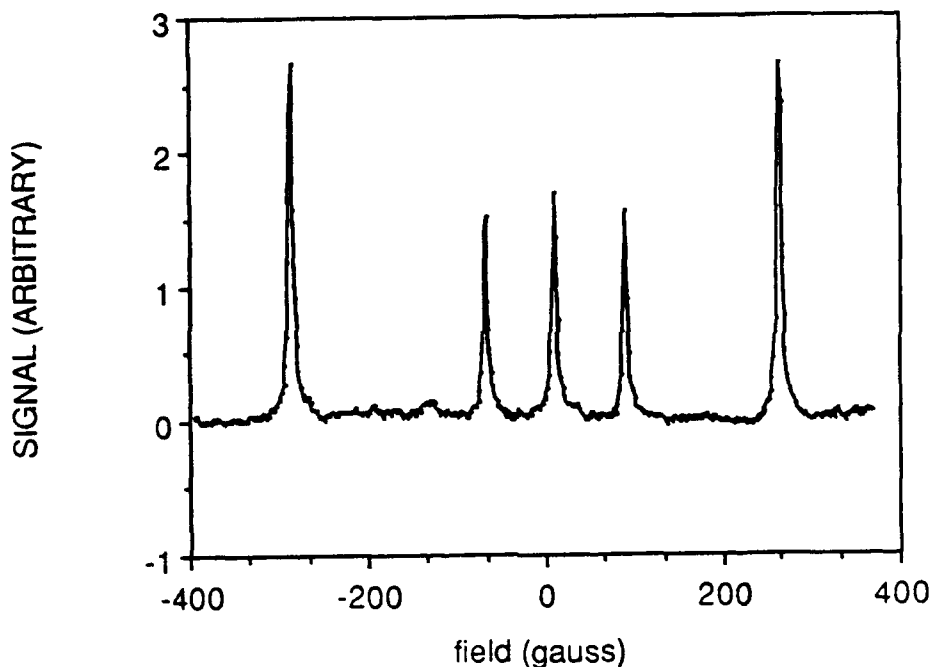


Figure 7

The ESR spectral intensity (in arbitrary units) from a D-T sample at 1.6 K is plotted as a function of the applied magnetic field. Five resonance lines are clearly visible resulting from the hyperfine splitting. T atoms produce the doublet hyperfine structure in the center of the T doublet.

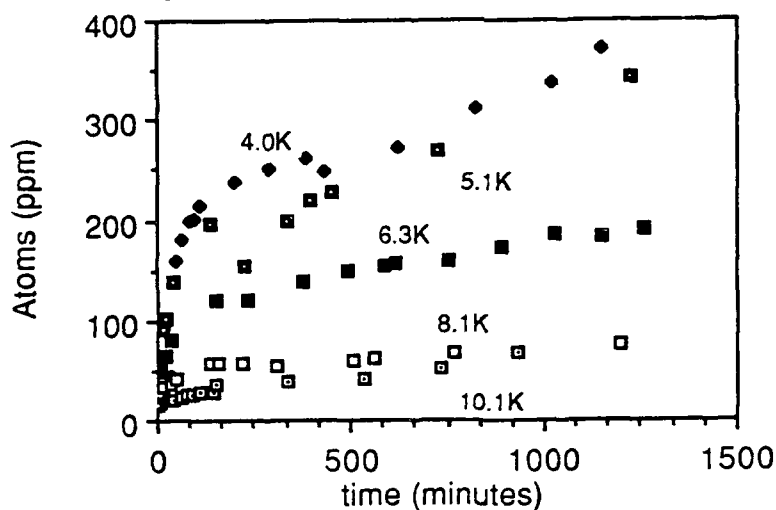


Figure 8

The atom concentration (in parts per million) in T_2 is plotted as a function of time for selected temperatures. The concentrations were obtained from an integral of the ESR data. The open squares containing a dot represent data taken at 10.1 K; the open squares represent data taken at 8.1 K; the solid squares represent data taken at 6.3 K; squares around diamonds represent data taken at 5.1 K; while the filled diamonds represent data taken at 4.0 K. In general, the concentration increases with decreasing temperature.

$$\Delta\omega = C_{\text{atom}}\omega_8 \quad (14)$$

where ω_8 is derived from the average local field and is calculated from the statistical nature of the problem. Even though the estimates of ω_8 vary considerably, an atom concentration of 1000 PPM will produce a linewidth of order 1 gauss, the experimentally observed value for T atoms in T_2 .

We reconcile this discrepancy by pointing out that the atoms observed by the ESR technique are "isolated" in the sense that they cannot have a near neighbor that has an unpaired electron spin or the local magnetic field contribution would give the atom a frequency address that is outside the observed ESR line (and in the noise).

Thus the ESR experiments are extremely valuable for understanding atoms in hydrogen hosts provided it is recognized that those atoms that are seen directly are isolated so that not all atoms are observed.

Relationship of the Optical Emission to Recombination. Hydrogen hosts containing tritium "glow in the dark". This was chronicled years ago by P. Clark Souers but more recently was the subject of a manuscript by Mapoles et al from LLNL[19]. This optical emission increases in intensity as the temperature is lowered in manner much like the steady state atom population. This is shown in Figure 9 where the atom density inferred from the ortho to para conversion experiments is plotted along with the relative intensity of the "steady state" glow from a solid T_2 sample. Note how similarly the two quantities scale with temperature.

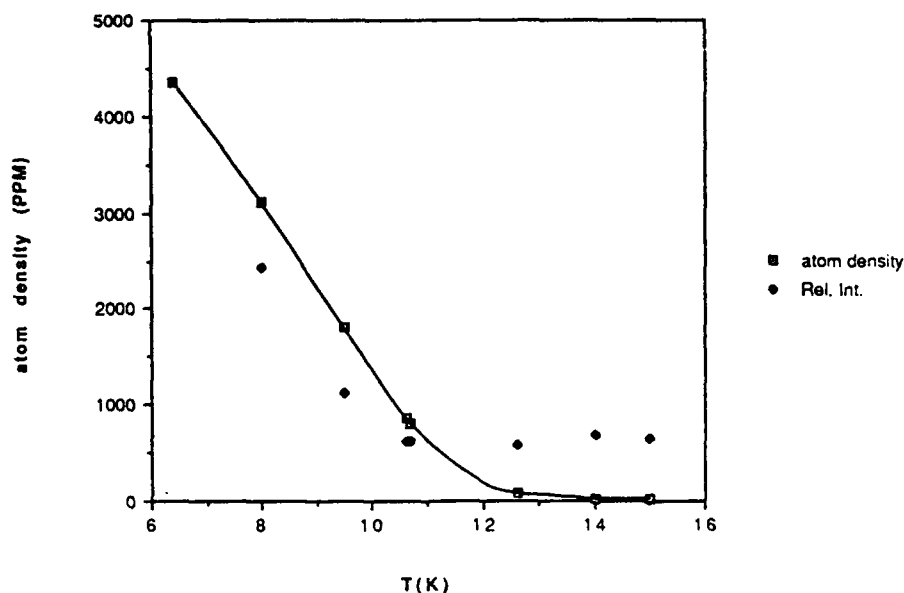


Figure 9

The atom concentration (in parts per million) is plotted as a function of time temperature in order to compare the relative concentration obtained from the glow in the optical experiments (filled diamonds) to the concentration derived from the o-p conversion experiments (open squares interpolated by a solid curve).

In addition, when a heat spike is triggered, the system emits a light pulse. The

spectral content of this pulse and its intensity in terms of the atom density are unknown at present. This observation does serve to focus attention on the microscopic processes of atom production (and the steady-state glow) and recombination (light pulses).

Recent Modeling work. This work had been performed in collaboration with Peter A. Fedders, Department of Physics, Washington University, St. Louis, Missouri.

Webeler, at NASA Lewis, studied H_2 containing small amounts of T_2 but he didn't use ESR techniques. He studied the heat released when atoms recombined in the host solid and attempted to quantify "storage times" for the energy resident in trapped atoms, again produced by the Webeler experiments. We will examine Rosen's approach.

In his most general approach, Rosen treated two types of atoms, "mobile atoms" and "trapped atoms" with atom diffusion included. Mobile atoms were produced by the beta decay of tritium but these atoms could become trapped in the solid leading to the second type of atom. Either type of atom represented stored energy. Diffusion was considered but then discarded because it complicated the analysis and didn't seem to be required to explain the experiments. Estimates were made of all the pertinent parameters and recombination was treated by gas-phase calculations of the cross-section leading to a temperature independent recombination coefficient ($\alpha = 1.3 \times 10^{-15} \text{ cm}^3/\text{s}$.) If Rosen's model is reduced to one type of atom, say the trapped atoms, and diffusion is ignored, the atom density would obey a rate equation given previously in equation 11. In this equation would predict a steady-state atom population that would grow at lower temperature due to the reduction in recombination as given by equation 12.

Starting from zero atom density the atom density grows according to:

$$m(t) = m_s \left[\tanh \left(\frac{t}{\tau} \right) \right] \quad (15)$$

where $\frac{t}{\tau} = \sqrt{2\alpha K}$.

It is not easy to adapt Rosen's treatment to explain ESR experiments. Are both the trapped and mobile atoms seen there? Which group is being observed? Although Rosen's model is valuable in understanding the heat released in Webeler's experiments and points out the critical role of coupling between the sample and the refrigerator, the parameters used there do not represent realistic estimates of known experimental observations.

First, the recombination coefficient was directly measured by Leach where he found that $\alpha = 6.0 \times 10^{-21} \text{ cm}^3/\text{s}$ at 6.75 and rapidly decreasing with temperature. Russian data, interpreted by Souers, would lead to value of $\alpha = 1.5 \times 10^{-24} \text{ cm}^3/\text{s}$ at 2 K and $\alpha = 7.5 \times 10^{-25} \text{ cm}^3/\text{s}$ at 1.4 K. Therefore in the temperature range of interest in Webeler experiments, the recombination used by Rosen differs from the estimates made in solid state by *nine orders of magnitude*. Indeed for a recombination coefficient of the magnitude used by Rosen, the observed atom density that participated in a triggered energy release could not be established for the atom production term he used.

Secondly, Rosen estimated the volume for trapping of the atoms and multiplied that volume by the beta decay rate to compare with the actual volume of the sample. Since his calculated volume per second receiving new mobile H atoms was comparable to the sample volume, he concluded that it was appropriate to consider the volumetric rate of production of mobile H to be approximately constant uniform throughout the H_2 sample. In our new model, where the parameters are obtained from other experiments where possible, we obtain a much smaller trapping volume that leads to a fraction of the sample receiving new atoms of only about 10 PPM per second for the decay rate appropriate to pure T_2 solid! In this case, it is not appropriate to consider the atom production to be uniform and we treat atom production differently.

We have proposed a new model that is simpler in some respects but more complicated in others than Rosen's. Our model attempts to explain the ESR experiments (that he was not addressing) and draws upon other experiments such as the measurements of the ortho-para conversion rate in solid T_2 for its parameters.

The pertinent features of this model are: (1) a new approach to atom production leads to a different time dependence of the atom density at fixed temperature; (2) a new interpretation of the EPR results is made possible; (3) the model has predictive ability, it can give an upper bound for maximum atom density for a specified production process; and (4) it can guide experiments attempting to make large atom that can be stored in molecular solids-- at temperatures and fields of practical interest,

SUGGESTIONS FOR FUTURE WORK

The experiments proposed here for future studies will directly measure the energy stored in the solid host by "thermal analysis"; the ratio of the light energy emitted during recombination to the total energy released; the magnetic susceptibility of the atoms (plus any other magnetic excitations); the times for atom equilibration following a triggered energy release; and the effects of a magnetic field on the energy storage times. *An alternative method of producing atoms in solid hydrogen will be explored.* Electron bombardment of hydrogen samples should be attempted. A search through the "parameter space" of magnetic field (H) and temperature (T) should be made in order to optimize the equilibrium density of atoms that can be stored in molecular solids-- at temperatures and fields of practical interest.

Thermal Analysis Experiments

The goal of the thermal analysis experiments is to measure the energy stored in zero applied magnetic field. Atom for the thermal analysis experiments can be produced in the sample by doping small amounts of T_2 into the H_2 to produce a steady-state atom density. The number of atoms produced per unit time will be directly proportional to the T_2 concentration. By varying the concentration of T_2 in H_2 , we can vary the source strength. Temperatures from 14 K to 2 K can be produced by varying the coupling of the sample chamber to a helium bath whose temperature can be regulated from 4.2 K to below 2 K.

The combined system ("system") consisting of molecular hydrogen host (H_2) and

single hydrogen (H) atoms is metastable and if considered to be a thermodynamic system, possesses a negative heat capacity at low temperatures. This metastability has been observed through "heat spikes" and light pulses that are either spontaneous or triggered by a positive temperature ramp.

By carefully designing the experiment, it will be possible to extract quantitative information about this system. A single set of thermal measurements cannot answer all the important questions since it is now known that a significant fraction of the energy stored during a triggered energy release will be calculated from the time dependence of the sample cell temperature.

The thermal analysis experiment will be direct probe of the stored energy in an H₂ host provided energy released as light is also measured and accounted for. It will also yield the atom density responsible for the second stored energy assuming all the energy is stored in forms of atoms.

If part of the recombination energy is released as light, then only that portion of energy that is heat or light absorbed by the sapphire cell (and H₂) will contribute to the measured "stored energy". After completing a series of experiments measuring the stored energy as a function of temperature, we could place an absorbent shield over the sample cell to trap emitted light and re-measure the stored energy as a function of the temperature. Comparison of the two sets of data would permit us to estimate how much light energy is emitted during triggered energy releases.

This estimate could be very important for future engineering studies. Although some light resulting from recombination is not surprising, there is a possibility that a very significant fraction of the total energy released is light. As noted earlier, Webeler noted that his samples reached steady-state temperature impossible to reach (from his known cooling power) based on the calculated beta-activity for his doped samples. He estimated that only one-fourth of the expected heat (from the beta decay) was being generated. We have made a similar (crude) estimate of the heat released but a more carefully designed experiment, such as the one we are proposing, is needed before any confidence can be attached to these estimates.

Magnetization Measurements

The goal of the magnetization measurements is to measure the atom as a function of applied magnetic field. In a separate set of experiments, the static magnetization and the magnetic susceptibility (χ) could be measured: (i) first in a fields below 1 Tesla; and (ii) in fields up to 8 Tesla. The magnetic susceptibility measurement is "not resonant" will pick up contributions from all electron spins in the sample not just the atoms. Attempts could be made to measure the transient response of the magnetization following a triggered energy release as that can provide an estimate of the recombination coefficient on the field. Details are given below.

Measurement of a sample's magnetization can yield valuable information regarding its structure, physical characteristics, or density of magnetic moments. In the case of solid hydrogen host containing atoms and other fragments of molecules (such as ions and electrons, magnetic moments are found on atoms, ions, electrons and even certain molecules that have nuclear magnetic moments. Because the nuclear magnetic moment

is approximately 2000 times smaller than the electron magnetic moment, we will ignore nuclear magnetism from the following discussion since the susceptibility depends on the square of magnetic moment so that for a sample with just a few parts per million (PPM) of atoms present, the electronic magnetic moment contributions will exceed those from nuclear moments.

Our experiment can have enough sensitivity to measure the susceptibility with a signal to noise ratio of approximately 25:1 at 4 K and 100:1 at K for 0.1% atom concentration. The magnetic susceptibility measurements could be extended to fields of 8 Tesla in order to measure the recombination coefficient as a function of field and temperature.

An Alternate Method of Atom Production

The goal of developing an alternate method of atom production is to avoid the use of tritium in atom production. The thrust of this project is to determine the conditions needed to store energy in solid hydrogen in quantities useful for combustion. Production of unpaired atoms in the solid by electron bombardment can lead to useful energy storage when recombination can be inhibited. Unfortunately, the mechanisms for producing unpaired atoms in the solid have not been studied in any detail and estimates are made based on data taken in the gas phase without direct measurements of atom concentrations.

When electrons are injected into solid hydrogen, the resulting radiation produces ions and excited molecules. Both species can produce atoms. Atoms are produced when the ions are neutralized and certain molecule excited states immediately decay into two atoms. If a monoenergetic beam of electrons energy is deposited in a very restricted region of the sample and the resulting high concentration of atoms in that region can recombine before the atom concentration becomes uniformly distributed in the sample. It is preferable to find an approach that produces the atoms uniformly in the solid.

We will use techniques now employed in Electron Energy Loss Spectroscopy (EELS) to quantify the energy loss electron energies, below 5 keV. This will establish the "range" versus energy and also distinguish between the atom production from ion recombination and molecular excitation in thin slabs of hydrogen. From this data, we can calculate an electron pulse shape $N(E)$, where $N(E)$ is the number of electrons per second with energy E , that will provide "uniform" dose to a macroscopic solid can be measured by calorimetry, using a heat pulse to trigger rapid recombination.

CONCLUSIONS

Due to the large scientific interest in spin polarized hydrogen in the last decade, there exists an available body of theoretical and experimental results valid for a gas atoms (with relatively high density) at low temperatures. While these results can serve as the starting point for understanding the behavior of "gas" of atoms embedded in a molecular solid host (or matrix).

Previous experimental and theoretical work on atoms in solid H_2 leads to the

conclusions: (i) that large concentrations of atoms can exist in molecular solids at low temperatures; (ii) that it is easier to cool samples with known radioactivity than might be imagined; (iii) that the atoms are inhomogeneously gesticulated throughout the sample; and (iv) that application of magnetic field may increase the concentration of atoms that can be stored at given temperature or their storage time.

Improved understanding of both atom production and recombination processes are needed before the result can be useful for engineering studies. The use of a long-lived radioactive isotope such as T_2 (half-life 12.3 years) to produce atoms in space applications is environmentally unacceptable. The goals of maximizing the stored energy and determining the conditions needed for storing the energy for a specific period of time are within reach.

REFERENCES

1. M. Blume, V. Emery, and R. Griffiths, Phys. Rev. A **4**, 1071 (1971).
2. R.W.H. Webeler, J. Chem. Phys. **64**, 2253 (1976).
3. R.K. Leach, A Paramagnetic Resonance Study of Hydrogen Atom Production and Recombination in Solid H_2 from 1.4 to 8 K, Thesis University of Wisconsin, Madison, Wisconsin (1972) [University Microfilms, Ann Arbor, Michigan (1972), No. 72-23060].
4. See, for example, J. Espenson, Chemical Kinetics and Reaction Mechanisms (McGraw-Hill, New York, 1981), pp. 168-169.
5. E. Lifshitz and L. Pitaevskii, Statistical Physics, Part 1 (Landau and Lifshitz Course of Theoretical Physics Vol. 5) (Pergamon, Oxford, 1980).
6. Gilbert W. Collins, Ph. D. Thesis, "A Magnetic Resonance Study of Atomic Excitations in Solid Hydrogen", The Ohio State University (1989).
7. J.R. Gaines, R.T. Tsugawa, and P.C. Souers, Phys. Rev. Lett. **42**, 1717 (1979).
8. J.R. Gaines, J.D. Sater, Evelyn Fearon, E.R. Mapoles, R.T. Tsugawa, P.C. Souers, and J.R. Gaines. Phys. Rev. Lett. **59**, 563 (1987).
9. G.W. Collins, P.C. Souers, E.M. Fearon, E.R. Mapoles, R.T. Tsugawa and J.R. Gaines, Phys. Rev. **B41**, 1816 (1990).
10. G.W. Collins, E.M. Fearon, J.L. Maienschein, E.R. Mapoles, R.T. Tsugawa, P.C. and J.R. Gaines. Phys. Rev. Lett. **65**, 444 (1990).
11. E.R. Mapoles, F. Magneto, G.W. Collins, and P.C. Souers, Phys. Rev. **B41**, 11653 (1990).
12. M. Sharnoff and R.V. Pound, Phys. Rev. **132**, 1003 (1963).
13. Gerald Rosen, J. Chem. Phys. **65**, 1735 (1976).
14. Gerald Rosen, J. Chem. Phys. **66**, 5423 (1977).
15. Frank J. Zeleznik, J. Chem. Phys. **65**, 4492 (1976).
16. J.R. Gaines, J.D. Sater, Evelyn Fearon, P.C. Souers, Fred E. McMurphy, and

Lett. **59**, 563 (1987).

17. Yue Cao, J.R. Gaines, Peter Fedders, and P.C. Souers, Phys. Rev. **B37**, 1474 (1988).

18. J.D. Sater, J.R. Gaines, E.m. Fearon, P.C. Souers, Fred E. McMurphy, and Evan R. Mapoles, Phys. Rev. **B37** 1482 (1988).

19. E.R. Mapoles, F. Magnotta, G.W. Collins, and P.C. Souers, Phys. Rev **B41**, 11653 (1990).